Appendix I

Pretreatment Program Chemical Review

Introduction

It may be possible in limited cases to identify the toxic influent sources by comparing pretreatment program data on suspected sources to chemical-specific and toxicity data on the POTW effluent. The objective of the PPCR is to determine the sources of toxicity by comparing chemical data on industrial dischargers to toxicity data reported in the literature. The pretreatment program information should include flow and chemical monitoring data on the industrial users, descriptions and schedules of industrial production campaigns, and inventories of chemicals used in production. The final outcome of this review should be an improved understanding of the industries' processes and chemical usage, and the possible identification of sources of toxicity. Source identification through the PPCR approach has been successful in reducing effluent toxicity at POTWs with a limited number and type of industrial inputs (Diehl and Moore, 1987).

General Procedure

The main steps in a PPCR are to:

- Gather the pertinent pretreatment program data
- Compare the data to POTW effluent toxicity results and/or TIE data
- Identify potential influent source(s) of toxicity
- Evaluate and recommend a toxicity control option(s).

A brief description of each of these steps follows.

Collect Data on Industrial Users

Data on all categorical, significant non-categorical and other potential toxic dischargers (e.g., industrial users with local limits and RCRA and CERCLA inputs) should be collected. A list of pertinent information that should be considered in a PPCR is presented in Table 2-3. The data collection effort should include a survey of each industrial user, using the example checklist shown in Table I-1.

Information on chemicals that may be used in manufacturing processes can be obtained from the *Encyclopedia of Chemical Technology* (Kirk-Othmer, 1982). Although OSHA regulations require that information on hazardous chemicals is to be made available to the public on MSDSs, information on various "specialty" chemicals can be difficult to obtain. When data on a "specialty" chemical are not disclosed, a literature review can be performed to determine the chemical's acute toxicity and biodegradability. This information allows assumptions to be made concerning the biodegradability of the chemical at the POTW and the potential for the chemical to cause effluent toxicity. An initial indication of the possible toxic pollutants causing effluent toxicity can be made by comparing expected or actual effluent concentrations to toxicity values provided in the literature.

Compare PPCR Data to POTW Effluent Toxicity Results

Information on the magnitude, variability, and nature of the POTW effluent toxicity can be compared with the PPCR data to determine the sources(s) of possible problem chemicals. This comparison can be made using statistical analyses to determine if the variability in the source characteristics can be related to the variability in the POTW effluent toxicity. A description of data analysis techniques for comparing POTW and industry pretreatment data follows.

Two types of statistical analyses can be used to compare the pretreatment program chemical data and POTW effluent toxicity data: linear regression (Draper and Smith, 1966) and cluster analysis (Pielou, 1984; Romesburg, 1984).

Table I-1. PPCR Data Sheet

Industry Name
Notes:

Address
Notes:

Industrial Category (SIC Code)
Notes:

TRE Objectives
Notes:

Manufactured Products
Notes:

Chemicals Used
Notes:

Amounts (write on MSDS)
Notes:

MSDS	_____ All Attached	_____ Partial Available

Process in which chemical is used
(write on each MSDS)
Notes:

Aquatic toxicity/biodegradability information on all chemicals used. Review MSDS, supplier information, and literature	_____ None	_____ Some

Notes:

Engineering drawings of facility
Notes:

Production flowchart and line schematic	_____ Available	_____ No

Notes:

All floor and process drains with schematic	_____ Available	_____ No

Notes:

Wastewater pretreatment system schematic	_____ Available	_____ No

Notes:

Facility records
Notes:

Water usage, water bills	_____ Available	_____ No

Notes:

DMRs for 24 months	_____ Available	_____ No

Notes:

Pretreatment system operations data	_____ Available	_____ No

Notes:

Pretreatment system operator interview	_____ Available	_____ No

Notes:

Spill prevention control plan	_____ Available	_____ No

Notes:

RCRA reports, hazardous waste manifests	_____ Available	_____ No

Notes:

Linear regression analysis is used to find correlations among the variables in the data base and to relate changes in POTW effluent toxicity to the variables. A cluster analysis using pattern recognition software can weigh and evaluate the significance of toxics/toxicity correlations. The determination of concentration /response relationships through statistical analysis should not be considered as a definitive answer to toxicity tracking because of the complexity of the factors contributing to toxicity in POTW effluents.

The following example illustrates how a stepwise linear regression technique can be used in a PPCR assessment. The technique is used to identify how changes in several variables can impact the presence and variability of effluent toxicity. Table I-2 presents an example data sheet for a POTW serving one manufacturing plant. In this example, only a few POTW effluent industry variables were used in the linear regression analysis; however, additional variables also could be added in the regression analysis.

The following variables are the "X" variables:

Industry variables:

- LBS is the manufactured product per month (millions of pounds).
- INFLOW is the discharge flow based on water usage (mgd).

POTW effluent variables:

- OFLOW is the recorded effluent flow (mgd).
- COD is the chemical oxygen demand concentration (mg/L).
- BOD_5 is the biochemical oxygen demand concentration (mg/L).
- Cu is the copper concentration (mg/L).
- Cr is the chromium concentration (mg/L).
- Zn is the zinc concentration (mg/L).

The following variable is the "Y" variable:

- LC50 is the acute LC50 as percent effluent.

By applying standard stepwise linear regression, the variables OFLOW, BOD_5, Cr, and Cu were eliminated because they were insignificant to toxicity. Stepwise linear regression showed that the remaining (X) variables were significant as regressed versus (Y) LC50. This analysis indicated that Zn, COD, LBS, and INFLOW were correlated with POTW effluent toxicity.

Identify Source(s) of Toxicity

Based on the data analysis, a list of the possible contributors to effluent toxicity at the POTW can be developed. Sources of suspected toxicants should be selected based on toxicant loading calculations. Industrial users who contribute potentially toxic

Table I-2. Data Sheet for Regression Analysis

	Parameter								
Month	**LBS**	**INFLOW**	**OFLOW**	**COD**	**BOD_5**	**Cu**	**Cr**	**Zn**	**LC50**
Jan	0.80	1.2	1.0	30	10	0.73	0.02	1.6	20
Feb	1.01	1.5	1.2	33	11	0.61	0.02	1.9	20
Mar	1.20	1.7	1.4	41	15	0.78	0.02	2.0	18
Apr	1.25	1.7	1.5	39	14	0.65	0.02	1.6	18
May	1.16	1.6	1.4	30	12	0.66	0.02	1.5	22
Jun	0.90	1.2	1.0	28	11	0.68	0.02	1.4	30
Jul	0.90	1.2	0.9	25	10	0.71	0.02	1.8	40
Aug	1.20	1.6	1.4	23	9	0.72	0.02	1.9	38
Sep	1.30	1.8	1.6	25	15	0.69	0.02	2.0	40
Oct	1.27	1.7	1.4	26	18	0.72	0.02	2.1	33
Nov	1.10	1.6	1.4	30	17	0.71	0.02	1.9	28
Dec	0.90	1.2	1.0	40	21	0.75	0.02	2.0	22

loadings of suspected toxicants would be candidates for a toxicity control evaluation.

Recommend Toxicity Control Option(s)

Of the potential toxicity control options, toxic chemical substitution or elimination is usually the most pragmatic approach. Thus, a follow-up interview with the toxic discharger(s) should be conducted to develop information concerning techniques for the preferred use of problem chemicals. A list of useful interview questions is shown in Table I-3. These questions may enable the industry to identify problem areas and possible corrective actions in the use of toxic chemicals in manufacturing. Source control may include substitution or elimination of problem chemicals, flow reduction, equalization, spill control, and manufacturing process changes.

Table I-3. Summary of the PPCR Chemical Optimization Procedure

1. Objectives
   a. Optimize chemical usage amounts in production and water treatment processes.
   b. Optimize chemical structures in process chemicals ensuring biodegradability or detoxification is possible.
   c. Establish process controls over incoming raw materials, measuring possible toxic components. Example: corrosion-resistant finish put on steel by manufacturer that must be removed prior to part fabrication.
2. Strategy
   a. Determine the role of each chemical in the process. This is done by supplier interviews and review of data gathered during the initial survey. Ask the questions:

      Can less of this chemical be used?

      Has the optimum amount been determined for each process?

      Do other suppliers offer compounds that will perform as well at lesser concentrations?

      Is the compound in reality a part of the manufacturer's water treatment system and independent of product production?

      OBJECTIVE: Use less chemicals per pound of product produced.

   b. Discover the biodegradability and toxicity of the process chemical. This is done by supplier interview, review of MSDS information, and literature search. Suppliers may not want to supply exact chemical formulations. In this case, ask industry to request supplier to perform tests to develop needed data. Questions to ask:

      What are the components in the product?

      What is its aquatic toxicity?

      Is the product biodegradable?

      What is the rate of biodegradation or half-life?

      Are there other component chemicals on the market that meet manufacturing requirements, but are low in toxicity and highly biodegradable?

      OBJECTIVE: Use chemicals that will not create or contribute to toxicity problems.

   c. Establish process controls over incoming raw materials. Many raw materials have chemicals used in their manufacturing that are removed in the production of the final product. Many raw materials may have trace contaminants that may cause toxic problems. Questions to ask:

      What chemicals are used in the manufacturing of the raw material?

      What are the residual amounts of these raw material contaminants or by-products?

      Are there quality-control procedures that measure the amounts of these chemicals?

      What are the statistical process measures used in the monitoring of these chemicals in the raw materials?

Table I-3. Summary of the PPCR Chemical Optimization Procedure (continued)

If these chemicals are required to be removed before the raw materials can be used in manufacturing the final product, what purpose do the chemicals serve in raw material manufacturing?
Can they be eliminated?

Can they be made less toxic or more biodegradable?

OBJECTIVE: Understand all raw materials being used and encourage development of QA procedures to monitor toxic chemicals removed during processing.

3. Outcome of Investigations

   a. There will be a list of all chemicals used in processing and manufacturing of products. Included will be the amounts used, why the chemicals are used, and if optimization is being practiced.

   b. MSDS sheets for all chemicals used will be on file.

   c. A list of chemicals applied or used in the manufacturing of all raw materials will be on file under that raw material with the residual amounts noted if possible.

   d. There will be a list of all chemicals and raw materials purchased on a monthly basis and the amount of product produced.

   OBJECTIVE: Hard information to be used in data analysis.

4. Use of opportunities available due to past experience

   a. With experience in various industries, certain chemicals will become “known” as typically used in some process of manufacturing.

   b. These known compounds can be categorized and toxicity determinations made. Once found toxic, the first information the industry must supply to the POTW staff conducting the TRE is whether these chemicals are used in its manufacturing process, in raw materials, or in water treatment processes.

   c. Letters also are sent to raw material suppliers asking if these compounds are used in raw material production. If they are, the supplier is asked to submit prototype alternative raw materials that do not contain these compounds.

   d. This can be done at the beginning of the TRE for known problem chemicals. Indeed, control regulations also usually involve establishing limits for selected known toxics in industrial operations.

   e. What is accomplished by this process can be remarkable. First, the supplier is alerted that these compounds can cause his or her customers problems, resulting in a search for an alternative raw material source that is free of these objectionable chemicals. A successful market search reduces the market demand for contaminated or objectionable raw material.

5. Tests to help assess toxicity/biodegradability on speciality formulated chemicals and mixtures and to help evaluate competitive products

   a. BOD_5, BOD_{20}.

   b. BOD_5, BOD_{20} performed at LC50 concentration with toxicity test performed on settled effluent from test.

   c. COD before and after BOD_5, BOD_{20} at LC50, EC50 concentrations.

   d. Estimate biodegradability by using BOD_5 and COD tests and the calculation $(BOD_5 - COD)/COD \times 100$ of 10 or 20 mg/L solutions of chemical; this can be repeated at a 20-day BOD.

   e. Biomass inhibition tests (see detailed procedures given in Section 5).

   f. LC50 on products; screening dilutions 1–10,000 ppm.

   OBJECTIVE: Help industry determine relative biodegradability and toxicity of various raw materials, products, and by-products.

References

Diehl, R., and S. Moore. 1987. Case History: A North Carolina Municipal TRE. *Toxicity Identification/Reduction Evaluation Workshop, Water Pollution Control Federation Conference*, Philadelphia, Pennsylvania.

Draper and Smith. 1966. *Step-wise Multiple Regression: Applied Regression Analysis*. New York, New York: John Wiley and Sons.

Kirk-Othmer. 1982. *Encyclopedia of Chemical Technology*. New York, New York: Wiley Interscience.

Pielou. 1984. *Cluster Analysis Techniques: The Interpretation of Ecological Data.* New York: Wiley Interscience.

Romesburg, H.C. 1984. *Cluster Analysis for Researchers*. Lifetime Learning Publications. Gelmont, California.